Chapter 13 Advanced Gas Concepts

Note: Below working the problems of this chapter, you should familiarize yourself with Table 13.1, below.

13.1 VAN DER WAALS EQUATION

13.1 Identity the postulate of the kinectic molecular theory most closely identified with the van der Waals constant *a*, and explain the relationship. Repeat the procedure for the constant *b*.

- The constant *a* reflects the intermolecular attractions in real gases. The kinetic molecular theory postulates no intermolecular attractions, which is a good approximation in many cases. The constant *b* reflects the actual volume of the molecules themselves. The kinetic molecular theory postulates that the volume of the molecules is zero (or negligible), also sometimes a good approximation.

13.2 In the van der Waals equation

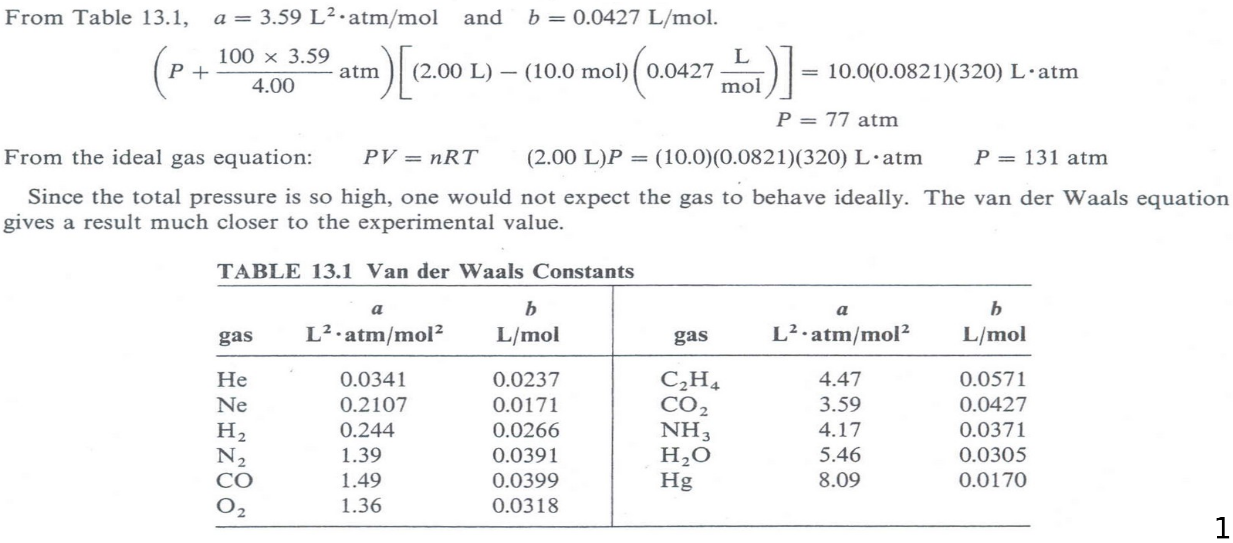
$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

The constant *a* accounts for what property of molecules of real gases?

- Intermolecular attraction

13.3 Using the Van der Waals equation, calculate the pressure exerted by 10.0 mol carbon dioxide in a 2.00 L vessel at 47 °C. Repeat the calculation using the equation of state for an ideal gas.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$



From Table 13.1, $a = 3.59\ \mathrm{L^2\cdot atm/mol}$ and $b = 0.0427\ \mathrm{L/mol}$.

$$\left(P + \frac{100 \times 3.59}{4.00}\ \mathrm{atm}\right)\left[(2.00\ \mathrm{L}) - (10.0\ \mathrm{mol})\left(0.0427\ \frac{\mathrm{L}}{\mathrm{mol}}\right)\right] = 10.0(0.0821)(320)\ \mathrm{L\cdot atm}$$

$$P = 77\ \mathrm{atm}$$

From the ideal gas equation: $PV = nRT$ $(2.00\ \mathrm{L})P = (10.0)(0.0821)(320)\ \mathrm{L\cdot atm}$ $P = 131\ \mathrm{atm}$

Since the total pressure is so high, one would not expect the gas to behave ideally. The van der Waals equation gives a result much closer to the experimental value.

TABLE 13.1 Van der Waals Constants

gas	*a* $\mathrm{L^2\cdot atm/mol^2}$	*b* L/mol	gas	*a* $\mathrm{L^2\cdot atm/mol^2}$	*b* L/mol
He	0.0341	0.0237	C_2H_4	4.47	0.0571
Ne	0.2107	0.0171	CO_2	3.59	0.0427
H_2	0.244	0.0266	NH_3	4.17	0.0371
N_2	1.39	0.0391	H_2O	5.46	0.0305
CO	1.49	0.0399	Hg	8.09	0.0170
O_2	1.36	0.0318			

Compare these results with the experimentally observed pressure of 82 atm.

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13.4 Calculate the pressure of 0.60 mol NH_3 gas in a 3.00 L vessel at 25°C (a) with the ideal gas law (b) with the van der Waals equation.

- $$(a)\quad P = \frac{nRT}{V} = \frac{(0.60\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(298\ \text{K})}{3.00\ \text{L}} = 4.9\ \text{atm}$$

  $$(b)\quad P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

  $$= \frac{(0.60\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(298\ \text{K})}{(3.00\ \text{L}) - (0.60\ \text{mol})(0.0371\ \text{L/mol})} - \frac{(0.60\ \text{mol})^2(4.17\ \text{L}^2\cdot\text{atm/mol}^2)}{(3.00\ \text{L})^2} = 4.8\ \text{atm}$$

13.5 Calculate the pressure of 15.00 mol neon at 30°C in a 12.0 L vessel using (a) the ideal gas law (b) the van der Waals equation.

- $$(a)\quad P = \frac{(15.00\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(303\ \text{K})}{12.0\ \text{L}} = 31.1\ \text{atm}$$

  $$(b)\quad P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

  $$= \frac{(15.00\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(303\ \text{K})}{(12.0\ \text{L}) - (15.00\ \text{mol})(0.0171\ \text{L/mol})} - \frac{(15.00\ \text{mol})^2(0.2107\ \text{L}^2\cdot\text{atm/mol}^2)}{(12.0\ \text{L})^2} = 31.4\ \text{atm}$$

13.6 (a) Under what sets of experimental conditions is the van der Waals equation more applicable than the ideal gas law equation? Calculate the pressure of 12.0 mol CO at 25°C in a 10.0 L vessel using (b) the ideal gas law (c) the van der Waals equation. Calculate the pressure of 0.120 mol CO at 25°C in a 10.0 L vessel using (d) the ideal gas law (e) the van der Waals equation.

- (a) the van der Waals equation is more applicable than the ideal gas equation (but still by no means exact) at high pressure and low temperature, where gases exhibit nonideal behavior. (Note that the van der Waals equation, like the ideal gas equation, is more precise at low pressures than at high pressures,) (*b*) $$P = \frac{(12.0\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(298\text{ K})}{10.0\text{ L}} = 29.4\text{ atm}$$

(*c*) $$P = \frac{(12.0\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(298\text{ K})}{(10.0\text{ L}) - (12.0\text{ mol})(0.0399\text{ L/mol})} - \frac{(12.00\text{ mol})^2(1.49\text{ L}^2\cdot\text{atm/mol}^2)}{(10.0\text{ L})^2} = 28.7\text{ atm}$$

(*d*) $$P = \frac{(0.120\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(298\text{ K})}{10.0\text{ L}} = 0.294\text{ atm}$$

(*e*) $$P = \frac{(0.120\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(298\text{ K})}{(10.0\text{ L}) - (0.120\text{ mol})(0.0399\text{ L/mol})} - \frac{(0.120\text{ mol})^2(1.49\text{ L}^2\cdot\text{atm/mol}^2)}{(10.0\text{ L})^2} = 0.294\text{ atm}$$

13.7 Using the van der Waals equation, calculate the pressure of 10.0 mol NH_3 gas in a 10.0 L vessel at 0 °C.

$$\left(P + n^2\frac{a}{V^2}\right)(V - nb) = nRT \qquad a = 4.2\text{ L}^2\cdot\text{atm/mol}^2 \qquad b = 0.037\text{ L/mol}$$

- $$\left[P + (10.0\text{ mol})^2\left(\frac{4.2\text{ L}^2\cdot\text{atm/mol}^2}{(10.0\text{ L})^2}\right)\right][(10.0\text{ L}) - (10.0\text{ mol})(0.037\text{ L/mol})] = nRT$$
  $$(P + 4.2\text{ atm})(9.6\text{ L}) = (10.0\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(273\text{ K}) \qquad P = 19.1\text{ atm}$$

13.8 What volume would 3.00 mol oxygen occupy at 50.0 atm pressure and 100 °C according to (a0 the ideal gas law (b) the van der Waals equation?

[Hint: Solve by successive approximations, using the volume obtained in part (a) in the pressure correction term to calculate a better answer in part (b). Use that answer to compute a still better answer, continuing until the results of two successive steps differ by a negligible amount.]

$$\left[P + (10.0\text{ mol})^2\left(\frac{4.2\text{ L}^2\cdot\text{atm/mol}^2}{(10.0\text{ L})^2}\right)\right][(10.0\text{ L}) - (10.0\text{ mol})(0.037\text{ L/mol})] = nRT$$
$$(P + 4.2\text{ atm})(9.6\text{ L}) = (10.0\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(273\text{ K}) \qquad P = 19.1\text{ atm}$$

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Putting this new value for V into the denominator of the first term on the right of the equation yields a value of V= 1.81 L. When the two successive values come out the same, the process is complete. (To check, use the value 1.81 L to calculate a value for P.)

13.9 According to the van der Waals equation, how many mol ammonia will occupy 7.00 L at 20.0 atm and 100 °C (See the hint in Problem 13.8)

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$$n = \frac{PV}{RT} = \frac{(20.0\ \text{atm})(7.00\ \text{L})}{(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(373\ \text{K})} = 4.57\ \text{mol}$$

Inserting this value into the van der Waals equation in the form

$$n = \left(P + \frac{n^2a}{V^2}\right)\left(\frac{V - nb}{RT}\right) = \frac{\left[\left(20.0 + \frac{(4.57)^2(4.17)}{(7.00)^2}\right)\text{atm}\right]\{[7.00 - (4.57)(0.0371)]\ \text{L}\}}{(0.0821)(373)\ \text{L}\cdot\text{atm/mol}} = 4.86\ \text{mol}$$

substituting the 4.86 mol for n in two places on the right side of the same equation and solving yields a value of 4.90 mol. Substituting 4.90 mol then yields a value 4.91 mol. Substituting this value again yields a value of 4.91 mol, which is the solution.

13.10 For a given number of moles of gas, show that the van der Waals equation predicts greater deviation from ideal behavior (a) at high temperature rather than low pressure at a given temperature, (b) at low temperature rather than a high temperature at given pressure.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad \text{compared to} \quad PV = nRT$$

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(a) At high pressure, the volume is low. Hence the n^2a/V^2 term is more important than at low pressure and high volume. (The square term makes the change in pressure more important for n^2a/V^2 than for P.) the constant nb term is also more important when subtracted from thee smaller V. (b) At low temperatures and a given pressure, V must be low, and the effect is as in part (a).

13.11 Assuming ideal behavior, calculate the volume per mol of gaseous water at 1.00 atm ppressure and 100 °C. Also calculate the volume of 1.00 mol liquid water at 100 °C (density = 0.958 g/mL). Assuming that this value is the totol volume of the molecules themselves, with negligible space between molecules, calculate the percent of the total volume of gaseous water at 100 °C which is “freevolume.”Compare the volume of 1.00 mol water molecules at 100 °C to the value of the van der Waals constant b for water (Table 13.1). Suggest a reason for the difference.

For the gas: $V = \frac{nRT}{P} = \frac{(1.00\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(373\text{ K})}{1.00\text{ atm}} = 30.6\text{ L}$

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For the liquid: $V = \text{mass/density} = (18.0\text{ g})/(0.958\text{ g/mL}) = 18.8\text{ mL}$

The percentage of the volume occupied is $\left(\frac{18.8\text{ mL}}{30{,}600\text{ mL}}\right)(100\%) = 0.0614\%$

The percentage of free volume is $(100.0000\%) - (0.0614\%) = 99.9386\%$

13.12 Compare the values of the van der Waals constants for NH_3 and N_2. Explain why the value of a is larger for NH_3 but that of b is larger for N_2.

- The constant a is related to intermolecular forces; those for NH_3 are much higher because of hydrogen bonding. The constant b is related to molecular volume. The hydrogen atoms of NH_3 take up practically no volume, and ammonia is little over half the volume of N_2.

13.13 According to the ideal gas law, at constant volume the pressure of a gas becomes zero at 0 K and is independent of the volume. Solve the van der Waals equation explicitly for pressure. Is the variation of pressure of a real gas with temperature at constant volume independent of the volume? Using the data of Table 13.1, determine the absolute temperature at which 1.0 mol helium gas in a volume of 1.0 L would have zero pressure. Repeat

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

the calculation for ethylene, C_2H_4. Compare these temperatures with the normal boiling points of He and C_2H_4.

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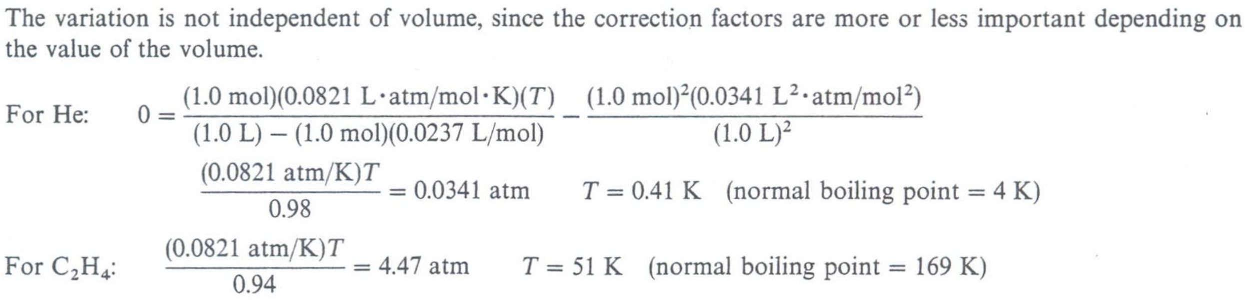

The variation is not independent of volume, since the correction factors are more or less important depending on the value of the volume.

For He: $$0 = \frac{(1.0\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(T)}{(1.0\ \text{L}) - (1.0\ \text{mol})(0.0237\ \text{L/mol})} - \frac{(1.0\ \text{mol})^2(0.0341\ \text{L}^2\cdot\text{atm/mol}^2)}{(1.0\ \text{L})^2}$$

$$\frac{(0.0821\ \text{atm/K})T}{0.98} = 0.0341\ \text{atm} \qquad T = 0.41\ \text{K} \quad (\text{normal boiling point} = 4\ \text{K})$$

For C_2H_4: $$\frac{(0.0821\ \text{atm/K})T}{0.94} = 4.47\ \text{atm} \qquad T = 51\ \text{K} \quad (\text{normal boiling point} = 169\ \text{K})$$

13.14 Expand the van der Waals equation (for 1 mol gas) into a cubic equation with respect to the volume. At the critical temperatureT_c, and the critical pressure P_c, the volume of 1 mol is the critical volume V_c. from this, obtain expression for a and b in terms of critical data.

- $$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad PV + \frac{a}{V} - \frac{ab}{V^2} - bP = RT$$

  $$V^3 - \frac{bP + RT}{P}V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

When P = P_c and T=T_c, this cubic equation must have the unique solution V=V_c. Hence the equation must be identical tp $(V-V_c)^3=V^3-3V^2V_c+3VV_c^2-V_c^3=0$.

Equating the coefficient of V^2 in the two forms:

$$\frac{bP_c + RT_c}{P_c} = 3V_c \qquad b = \frac{3V_cP_c - RT_c}{P_c} = 3V_c - \frac{RT_c}{P_c}$$

Equating the coefficients of V:

$$\frac{a}{P_c} = 3V_c^2 \qquad a = 3V_c^2P_c$$

Equating the coefficients of V^0:

$$V_c^3 = \frac{ab}{P_c} \qquad ab = V_c^3P_c \qquad a = 3V_c^2P_c\ \ (from\ above) \qquad b = \frac{1}{3}V_c$$

13.15 Expand the van der Waals equation (for n mol gas) into a cubic equation in V. Solve this equation to calculate the volume occupied by 3.00 mol oxygen at 50.0 atm pressure and 100 ℃. Compare the result with that obtained by successive approximation in Problem 13.8.

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=\ nRT$$

$$PV-Pnb+\frac{n^2a}{V}-\frac{n^3ab}{V^2}=nRT$$

$$V^3-(\frac{nRT}{P}+nb)V^2+\frac{n^2a}{P}V-\frac{n^3ab}{P}=$$

An equation in the form $y^3+py^2+qy+r=0$ is converted into the equation $x^3+vx+w=0$ by the substitution $y=x-p/3$ where $v=\frac{1}{3}(3q-p^2)$ and $w=\frac{1}{27}(2p^3-9pq+27r)$. Using the further substitutions $A=\sqrt[3]{-\frac{w}{2}+\sqrt{\frac{w^2}{4}+\frac{w^3}{27}}}$ and $B=\sqrt[3]{-\frac{w}{2}-\sqrt{\frac{w^2}{4}+\frac{w^3}{27}}}$ three possible solutions are obtained:

$$x=A+B \qquad x=-\frac{A+B}{2}+\sqrt{-3}\left(\frac{A-B}{2}\right) \qquad x=-\frac{A+B}{2}-\sqrt{-3}\left(\frac{A-B}{2}\right)$$

For the given data,

$$q=\frac{n^2a}{P}=\frac{(3.00)^2(1.36)}{50.0}=0.245$$

Then

$$v=\tfrac{1}{3}(3(0.245)-(-1.93)^2)=-0.997$$

$$w=\tfrac{1}{27}[2(-1.93)^3-9(-1.93)(0.245)+27(-0.02335)]=-0.398$$

$$A=\sqrt[3]{-\left(\frac{-0.398}{2}\right)+\sqrt{\frac{(0.398)^2}{4}+\frac{(-0.997)^3}{27}}}=0.632$$

$$B=\sqrt[3]{0.199-0.0539}=0.525$$

$$x=A+B=0.632+0.525=1.157 \quad \text{(the other solutions for } x \text{ are imaginary)}$$

$$y=1.157-(-1.93/3)=1.80\text{ L}$$

This value is very close to that found in Problem 13.8. Indeed, it is not worth the extra effort to obtain an “exact” solution with the cubic equation, since the van der Waals equation itself is far from exact.